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(54) Liquid cleaning compositions.

(57) A substantially non-aqueous liquid cleaning composition comprises a non-aqueous liquid phase and dispersed solids which comprise an inorganic percarbonate bleach and a bleach precursor, wherein the precursor has a molar solubility in the liquid phase alone multiplied by the number of active groups of no more than 1.2 mmol per 100 ml at 25 °C.

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The present invention relates to liquid cleaning compositions, in particular to substantially non-aqueous liquid detergent compositions. Non-aqueous liquid detergent compositions are those containing little or no water.

Non-aqueous compositions are generally preferred when it is desired to incorporate bleach, because the water in aqueous compositions causes instability of the bleach.

In the application of fabrics washing, the oxygen bleaches are preferred, for example in the form of an inorganic persalt, preferably with a bleach precursor.

In the case of the inorganic persalt bleaches, the precursor makes the bleaching more effective at lower temperatures, i.e. in the range from ambient temperature to about 60°C, so that such bleach systems are commonly known as low-temperature bleach systems and are well-known in the art. The inorganic persalt such as sodium perborate, either the monohydrate or the tetrahydrate, acts to release active oxygen in solution, and the precursor is usually an organic compound having one or more reactive acyl residues, which cause the formation of peracids, the latter providing for a more effective bleaching action at lower temperatures than the peroxybleach compound alone.

Recent concern about the impact of boron-containing compounds on the environment have lead to a desire to replace sodium perborate by an alternative inorganic persalt. Of these, the percarbonates are particularly desirable. After release of the active oxygen in the wash liquor, the resulting carbonates effectively act as builders, enabling a reduction in the amount of additional builder to be incorporated in the composition. Since most of the bleach, precursor and builder materials are present in non-aqueous compositions in the form of dispersed solids, it is highly desirable to minimise their amounts of inclusion.

Generally speaking the less solids that are present, the better is the pourability of the composition and also its tendency to 'set' (i.e. solidify) is reduced.

Unfortunately, when percarbonates are used in non-aqueous liquid compositions in the presence of the most common precursors in current use, they demonstrate a pronounced instability. Examples of such common precursors are tetraacetyl ethylene diamine (TAED) and sodium nonanoyloxy benzene sulphonate (SNOBS).

The applicants have now found that considerable improvement in the stability of the bleach system, i.e. the percarbonate and/or the precursor, is obtained by using a precursor which is relatively insoluble in the non-aqueous liquid phase of the composition.

Therefore, the present invention provides a substantially non-aqueous liquid cleaning composition comprising a non-aqueous liquid phase and dispersed solids which comprise an inorganic percarbonate bleach and a precursor, wherein the precursor has a molar solubility in the liquid phase alone multiplied by the number of active groups of no more than 1.2 mmol per 100 ml at 25°C.

Preferably, the precursor has a molar solubility in the liquid phase alone multiplied by the number of active groups of no more than 0.2 mmol per 100 ml at 25°C.

The term 'active groups' has the following meaning. A conventional precursor such as TAED has four acetyl groups but only two of these react with the persalt to release active oxygen. Thus for, TAED only these two acetyl groups are the 'active' groups.

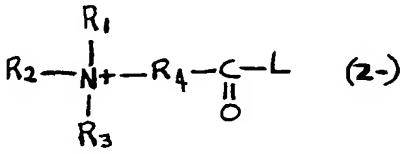
However the solubility of TAED alone is too high so that the resulting non-aqueous liquid compositions are outside the scope of the present invention.

In general, the percarboxylic acid precursors are usually preferred, rather than the percarbonic acid precursors.

Cationic precursors generally have low solubility in the liquid phase of such compositions.

The term cationic precursor includes amphoteric and zwitterionic species. Quaternary ammonium compounds are especially preferred cationic precursors.

Precursor compounds usable in the invention are quaternary ammonium precursors. Examples of these compounds are described in US 4,904,406 and have the general formula

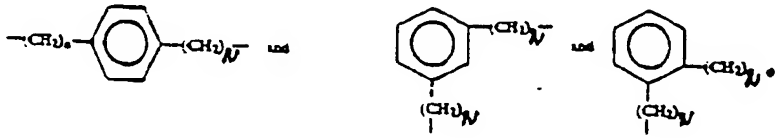


(Z-)

wherein

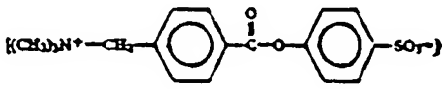
R_1, R_2 and R_3 are each a radical selected from the group consisting of optionally substituted alkyl, alkenyl,

hydroxyalkyl and polyoxyalkylene containing from 1 to 18 carbon atoms;
or two of R_1, R_2 and R_3 together with R_4 and the N-atom form an optionally substituted, nitrogen-containing heterocyclic ring system;
or two or more of R_1, R_2 and R_3 together with the N-atom form an optionally substituted, nitrogen-containing heterocyclic ring system;
R_4 (if not formed into a nitrogen-containing heterocyclic ring system together with R_1 and/or R_2 and/or R_3) is a bridging group selected from

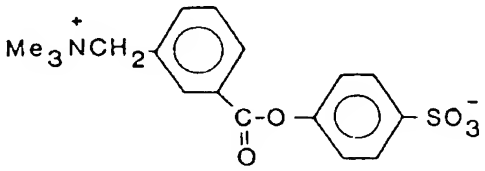


wherein
each n individually can be 0, 1 or 2;
L is a leaving group, the conjugate acid of which has a pK_a in the range of from 4 to 13, preferably from about 8 to 10; and
Z can be a chloride, bromide, hydroxide, nitrate, methosulphate, bisulphate, acetate, sulphate, citrate, borate or phosphate anion.

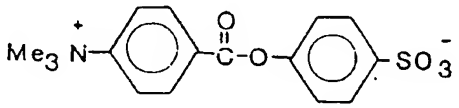
Of this class, particularly preferred is 1-[4-(N,N,N-trimethylammoniummethyl) benzoyloxy] benzene-4-sulphonate, that is, the compound of formula



(hereinafter called compound A).
Other suitable compounds of this class are:

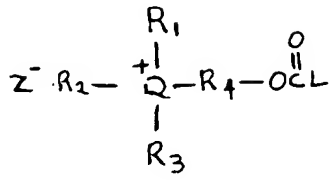


(hereinafter called compound D) and



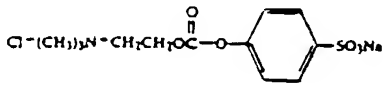
(hereinafter called compound E).

Another class of precursors are those disclosed in US 4,751,015, which have the general formula



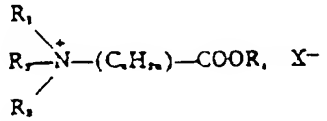
wherein:
R_1, R_2 and R_3 are each a radical selected from the group consisting of alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, alkaryl, aryl, phenyl, hydroxyalkyl, polyoxyalkylene and R_4OCOL;
or two or more of R_1, R_2 and R_3 together form an alkyl substituted or unsubstituted nitrogen-containing hetercyclic ring system;
or at least one of R_1, R_2 and R_3 is attached to R_4 to form an alkyl substituted or unsubstituted nitrogen-containing heterocyclic ring system;
R_4 is selected from the bridging group consisting of alkylene, cycloalkylene, alkylenephenylene, phenylene, arylene, and polyalkoxylene and wherein the bridging group can be unsubstituted or substituted with C_1 - C_{20} alkyl, alkenyl, benzyl, phenyl and aryl radicals;
Z is a monovalent or multivalent anion leading to charge neutrality when combined with Q+ in the appropriate ratio and wherein Z is sufficiently oxidatively stable not to interfere significantly with bleaching by a peroxy carbonic acid;
Q is nitrogen or phosphorous; and
L is a leaving group, the conjugate acid of which has a pK_a in the range of from about 6 to about 13.

One compound within the latter class is 2-(N,N,N-trimethylammonium)ethyl sodium 4-sulphophenyl carbonate which has the formula



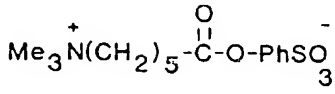
(hereinafter called compound B)

Other suitable quatenary ammonium precursors are those described in British Patent Specification GB 1382 594. These have the general formula



wherein $-(C_nH_{2n})-$ is an optionally branched chain having n equal to 3 or more;
R_1 is an optionally-substituted alkyl radical containing from 1 to 20 carbon atoms, alkaryl, optionally-substituted aryl or polyoxyalkylene radical;
R_2 and R_3 are each a lower alkyl or hydroxyalkyl radical; or two or more of R_1, R_2, R_3 together with the N-atom form an optionally-substituted nitrogen-containing heterocyclic ring system;
R_4 is an optionally-substituted phenyl group;
X is chlorine or bromine.

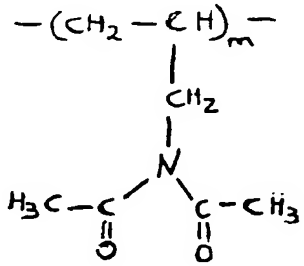
An example of this group is



(hereinafter called compound F).

Yet again, the precursor may be any of the organic amphoteric compounds described in European Patent Specification EP – A – 284 292.

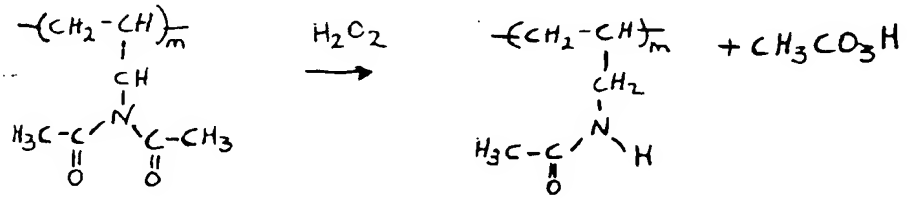
Another useful non – cationic precursor compound is a poly (diacetylallylamine), "PDAA", of the following molecular formula



(I)

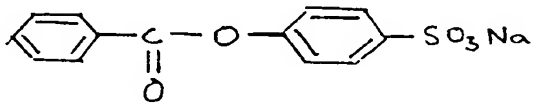
having molecular weight of from 500 to 1,000,000, preferably 600 to 750,000; for example from about 2500 to about 25,000, or from about 5,000 to about 15,000.

This compound will perhydrolyse forming peracetic acid according to the following reaction scheme:



These compounds are novel compounds and can be synthesised by the reaction of poly(allylamine) with acetic anhydride or isopropenyl acetate or they can be synthesised by polymerising diacetylallylamine, which monomer can be prepared by the reaction of allylamine with acetic anhydride or isopropenyl acetate.

The invention also includes compositions comprising only low solubility precursors which are not cationic. An example of such a precursor is sodium benzoyloxy benzene sulphonate which has the formula



(hereinafter called compound C) which is described in UK patent specification GB 839 715.

The ratio by weight of the peroxybleach compound to the precursor is from about 20:1 to about 2:1, preferably from about 10:1 to about 3.4:1. Whilst the amount of the bleach system, i.e. peroxybleach compound and precursor, may be varied between about 5% and about 35% by weight of the total liquid phase, it is preferred to use from about 6% to about 30% of the ingredients forming the bleach system. Thus, the preferred level of the peroxybleach compound in the composition is between about 5.5% and about 27% by weight, while the preferred level of the activator is between about 0.5% and about 14%, most preferably between about 1% and about 10% by weight.

Although any form of percarbonate bleach may be used, generally we prefer percarbonates of the kind described in European patent specification EP – A – 363 852. In their commercially available form, these percarbonates only contain about 7.5% available oxygen. Although they then have to be used at about double the rate of (say) a percarbonate with 15% available oxygen, they give improved stability and remove the necessity of adding extra carbonate for its builder effect.

BLEACH STABILIZERS

Whilst the bleach precursors are selected to improve the stability of the bleach system, it is also preferred to include in the compositions, a stabilizer for the bleach or bleach system, for example ethylene diamine tetramethylene phosphonate and diethylene triamine pentamethylene phosphonate or other appropriate organic phosphonate or salt thereof, such as the Dequest range hereinbefore described. These stabilisers can be used in acid or salt form, such as the calcium, magnesium, zinc or aluminium salt form. The stabilizer may be present at a level of up to about 1% by weight, preferably between about 0.1% and about 0.5% by weight.

PRODUCT FORM

All compositions according to the present invention are liquid cleaning products. In the context of this specification, all references to liquids refer to materials which are liquid at 25°C at atmospheric pressure. They may be formulated in a very wide range of specific forms, according to the intended use. They may be formulated as cleaners for hard surfaces (with or without abrasive) or as agents for warewashing (cleaning of dishes, cutlery etc) either by hand or mechanical means, as well as in the form of specialised cleaning products, such as for surgical apparatus or artificial dentures. They may also be formulated as agents for washing and/or conditioning of fabrics.

Thus, the compositions will usually contain at least one agent which promotes the cleaning and/or conditioning of the article(s) in question, selected according to the intended application. Usually, this agent will be selected from surfactants, enzymes, bleaches, microbiocides, (for fabrics) fabric softening agents and (in the case of hard surface cleaning) abrasives. Of course in many cases, more than one of these agents will be present, as well as other ingredients commonly used in the relevant product form.

Preferably the viscosity of compositions in accordance to the invention is less than 2,500 mPa.s at 21 s^{-1}, more preferably between 50 and 2,000, most preferably from 300 to 1,500.

SURFACTANT

Where surfactants are solids, they will usually be dissolved or dispersed in the liquid phase. Where they are liquids, they will usually constitute all or part of the liquid phase. However, in some cases the surfactants may undergo a phase change in the composition.

In general, surfactants for use in the compositions of the invention may be chosen from any of the classes, sub-classes and specific materials described in "Surface Active Agents" Vol. I, by Schwartz & Perry, Interscience 1949 and "Surface Active Agents" Vol. II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in "Tensid-Taschenbuch", H. Stache, 2nd Edn., Carl Hanser Verlag, München & Wien, 1981.

In respect of all surfactant materials, but also with reference to all ingredients described herein as examples of components in compositions according to the present invention, unless the context requires otherwise, the term "alkyl" refers to a straight or branched alkyl moiety having from 1 to 30 carbon atoms, whereas lower alkyl refers to a straight or branched alkyl moiety of from 1 to 4 carbon atoms. These definitions apply to alkyl species however incorporated (e.g. as part of an aralkyl species). Alkenyl (olefin) and alkynyl (acetylene) species are to be interpreted likewise (i.e. in terms of configuration and number of carbon atoms) as are equivalent alkylene, alkenylene and alkynylene linkages. For the avoidance of doubt, any reference to lower alkyl or C_{1-4} alkyl (unless the context so forbids) is to be taken specifically as a recitation of each species wherein the alkyl group is (independent of any other alkyl group which may be present in the same molecule) methyl, ethyl, iso-propyl, n-propyl, n-butyl, iso-butyl and t-butyl, and lower (or C_{1-4}) alkylene is to be construed likewise.

Preferably the total level of surfactants is from 5-75 % by weight of the composition, more preferably 15-60 %, most preferably 25-50 %.

NON-IONIC SURFACTANTS

Nonionic detergent surfactants are well-known in the art. They normally consist of a water-solubilizing polyalkoxylene or a mono- or di-alkanolamide group in chemical combination with an organic hydrophobic group derived, for example, from alkylphenols in which the alkyl group contains from about 6 to about 12 carbon atoms, dialkylphenols in which each alkyl group contains from 6 to 12 carbon atoms, primary,

secondary or tertiary aliphatic alcohols (or alkyl-capped derivatives thereof), preferably having from 8 to 20 carbon atoms, monocarboxylic acids having from 10 to about 24 carbon atoms in the alkyl group and polyoxypropylenes.

Also common are fatty acid mono- and dialkanolamides in which the alkyl group of the fatty acid radical contains from 10 to about 20 carbon atoms and the alkyloyl group having from 1 to 3 carbon atoms. In any of the mono- and dialkanolamide derivatives, optionally, there may be a polyoxyalkylene moiety joining the latter groups and the hydrophobic part of the molecule.

In all polyalkoxylene containing surfactants, the polyalkoxylene moiety preferably consists of from 2 to 20 groups of ethylene oxide or of ethylene oxide and propylene oxide groups. Amongst the latter class, particularly preferred are those described in the applicants' published European specification EP-A-225,654, especially for use as all or part of the liquid phase.

Also preferred are those ethoxylated nonionics which are the condensation products of fatty alcohols with from 9 to 15 carbon atoms condensed with from 3 to 11 moles of ethylene oxide. Examples of these are the condensation products of C11-13 alcohols with (say) 3 to 7 moles of ethylene oxide. These may be used as the sole nonionic surfactants or in combination with those of the described in the last-mentioned European specification, especially as all or part of the liquid phase.

Another class of suitable nonionics comprise the alkyl polysaccharides (polyglycosides/oligosaccharides) such as described in any of specifications US 3,640,998; US 3,346,558; US 4,223,129; EP-A-92,355; EP-A-99,183; EP 70,074, '75, '76, '77; EP 75,994, '95, '96.

Mixtures of different nonionic detergent surfactants may also be used. Mixtures of nonionic detergent surfactants with other detergent surfactants such as anionic, cationic or ampholytic detergent surfactants and soaps may also be used. Preferably the level of nonionic surfactants is from 5-75 % by weight of the composition, more preferably 15-60%, most preferably 25-50%.

ANIONIC SURFACTANTS

Examples of suitable anionic detergent surfactants are alkali metal, ammonium or alkylolamine salts of alkylbenzene sulphonates having from 10 to 18 carbon atoms in the alkyl group, alkyl and alkylether sulphates having from 10 to 24 carbon atoms in the alkyl group, the alkylether sulphates having from 1 to 5 ethylene oxide groups, and olefin sulphonates prepared by sulphonation of C10-24 alpha-olefins and subsequent neutralization and hydrolysis of the sulphonation reaction product.

All ingredients before incorporation will either be liquid, in which case, in the composition they will constitute all or part of the liquid phase, or they will be solids, in which case, in the composition they will either be dispersed in the liquid phase or they will be dissolved therein. Thus as used herein, the term "solids" is to be construed as referring to materials in the solid phase which are added to the composition and are dispersed therein in solid form, those solids which dissolve in the liquid phase and those in the liquid phase which solidify (undergo a phase change) in the composition, wherein they are then dispersed.

THE NON-AQUEOUS ORGANIC SOLVENT

As a general rule, the most suitable liquids to choose as the liquid phase are those organic materials having polar molecules. In particular, those comprising a relatively lipophilic part and a relatively hydrophilic part, especially a hydrophilic part rich in electron lone pairs, tend to be well suited. This is completely in accordance with the observation that liquid surfactants, especially polyalkoxylated nonionics, are one preferred class of material for the liquid phase.

Non-surfactants which are suitable for use as the liquid phase include those having the preferred molecular forms referred to above although other kinds may be used, especially if combined with those of the former, more preferred types. In general, the non-surfactant solvents can be used alone or with in combination with liquid surfactants. Non-surfactant solvents which have molecular structures which fall into the former, more preferred category include ethers, polyethers, alkylamines and fatty amines, (especially di- and tri-alkyl- and/or fatty- N-substituted amines), alkyl (or fatty) amides and mono- and di- N-alkyl substituted derivatives thereof, alkyl (or fatty) carboxylic acid lower alkyl esters, ketones, aldehydes, and glycerides. Specific examples include respectively, di-alkyl ethers, polyethylene glycols, alkyl ketones (such as acetone) and glyceryl trialkylcarboxylates (such as glyceryl tri-acetate), glycerol, propylene glycol, and sorbitol.

Many light solvents with little or no hydrophilic character are in most systems unsuitable on their own Examples of these are lower alcohols, such as ethanol, or higher alcohols, such as dodecanol, as well as alkanes and olefins. However, they can be combined with other liquid materials.

PROPORTION OF LIQUID PHASE

The liquid phase (whether or not comprising liquid surfactant) is present in an amount of at least 10% by weight of the total composition. The amount of the liquid phase present in the composition may be as high as about 90%, but in most cases the practical amount will lie between 20 and 70% and preferably between 35 and 50% by weight of the composition.

SOLIDS CONTENT

In general, the solids content of the product may be within a very wide range, for example from 10 - 90%, usually from 30 - 80% and preferably from 50 - 65% by weight of the final composition. The solid phase should be in particulate form and have an average particle size of less than 300 μm, preferably less than 200 μm, more preferably less than 100 μm, especially less than 10 μm. The particle size may even be of sub - micron size. The proper particle size can be obtained by using materials of the appropriate size or by milling the total product in a suitable milling apparatus. In order to control aggregation of the solid phase leading to unredispersible settling or setting of the composition, it is preferred to include a deflocculant therein.

OTHER INGREDIENTS

In addition to the components already discussed, there are very many other ingredients which can be incorporated in liquid cleaning products.

There is a very great range of such other ingredients and these will be choosen according to the intended use of the product. However, the greatest diversity is found in products for fabrics washing and/or conditioning. Many ingredients intended for that purpose will also find application in products for other applications (e.g. in hard surface cleaners and warewashing liquids).

DETERGENCY BUILDERS

The detergency builders are those materials which counteract the effects of calcium, or other ion (water hardness), either by precipitation or by an ion sequestering effect. They comprise both inorganic and organic builders. They may also be sub - divided into the phosphorus - containing and non - phosphorus types, the latter being preferred when environmental considerations are important.

In general, the inorganic builders comprise the various phosphate -, carbonate -, silicate -, borate - and aluminosilicates - type materials, particularly the alkali - metal salt forms. Mixtures of these may also be used.

Examples of phosphorus - containing builders, when present, include the water - soluble salts, espe - cially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hex - ametaphosphates.

Examples of non - phosphorus - containing inorganic builders, when present, include water - soluble alkali metal carbonates, bicarbonates, borates, silicates, metasilicates, and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and zeolites.

Examples of organic builders include the alkali metal, ammonium and substituted ammonium, citrates, succinates, malonates, fatty acid sulphonates, carboxymethoxy succinates, ammonium polyacetates, car - boxylates, polycarboxylates, aminopolycarboxylates, polyacetyl carboxylates and polyhydroxysulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarbox - ylic acids and citric acid. Other examples are organic phosphonate type sequestering agents such as those sold by Monsanto under the tradename of the Dequest range and alkanehydroxy phosphonates.

Other suitable organic builders include the higher molecular weight polymers and co - polymers known to have builder properties, for example appropriate polyacrylic acid, polymaleic acid and polyacrylic/ polymaleic acid co - polymers and their salts, such as those sold by BASF under the Sokalan Trade Mark.

Preferably the level of builder materials is from 1 to 40% by weight of the composition, more preferably 5 - 40% by weight.

STABILISERS

To keep the solids in dispersion, it is usually preferred to incorporate one or more agents to stabilise the rheology of the compositions. Such stabilisers include materials to inhibit settling of the solid particles and so minimise clear layer formation. Examples of such materials are highly voluminous metal and metalloid oxides such as described in UK Patent Specification GB 1 205 711. Another suitable class stabilisers of this type comprises the hydrophobically modified silicas.

Another type of stabiliser is a deflocculant. Deflocculants inhibit the aggregation of particulate solids which could both accelerate sedimentation and ultimately lead to setting (gelling or solidification).

Therefore compositions of the present invention preferably also comprise a deflocculant material. In principle, any material may be used as a deflocculant provided it fulfils the deflocculation test described in European Patent Specification EP-A-266199 (Unilever). The capability of a substance to act as a deflocculant will partly depend on the solids/liquid phase combination. However, especially preferred are acids.

"Fatty" anions are very suitable deflocculants, and a particularly preferred class of deflocculants comprises anionic surfactants. Although anionics which are salts of alkali or other metals may be used, particularly preferred are the free acid forms of these surfactants (wherein the metal cation is replaced by an H+ cation, i.e. proton). These anionic surfactants include all those classes, sub-classes and specific forms described in the aforementioned general references on surfactants, viz, Schwartz & Perry, Schwartz Perry and Berch, McCutcheon's, Tensid-Taschenbuch; and the free acid forms thereof. Many anionic surfactants have already been described hereinbefore. In the role of deflocculants, the free acid forms of these are generally preferred.

In particular, some preferred sub-classes and examples are the C10-C22 fatty acids and dimers thereof, the C8-C18 alkylbenzene sulphonic acids, the C10-C18 alkyl- or alkylether sulphuric acid monoesters, the C12-C18 paraffin sulphonic acids, the fatty acid sulphonic acids, the benzene-, toluene-, xylene- and cumene sulphonic acids and so on. Particularly preferred are the linear C12-C18 alkylbenzene sulphonic acids.

As well as anionic surfactants, zwitterionic-types can also be used as deflocculants. These may be any described in the aforementioned general surfactant references. One example is lecithin.

The level of the deflocculant material in the composition can be optimised by the means described in the aforementioned EP-A-266199, but in very many cases is at least 0.01%, usually 0.1% and preferably at least 1% by weight, and may be as high as 15% by weight. For most practical purposes, the amount ranges from 2-12%, preferably from 4-10% by weight, based on the final composition.

MISCELLANEOUS OTHER INGREDIENTS

Other ingredients comprise those remaining ingredients which may be used in liquid cleaning products, such as fabric conditioning agents, enzymes, perfumes (including deoperfumes), micro-biocides, colouring agents, fluorescent agents, soil-suspending agents (anti-redeposition agents), corrosion inhibitors, enzyme stabilising agents, bleach catalysts and lather depressants.

Amongst the fabric conditioning agents which may be used, either in fabric washing liquids or in rinse conditioners, are fabric softening materials, quaternary ammonium salts, imidazolinium salts, fatty amines, cellulases and clays.

Enzymes which can be used in liquids according to the present invention include proteolytic enzymes, amylolytic enzymes and lipolytic enzymes (lipases). Various types of proteolytic enzymes, lipolytic enzymes and amylolytic enzymes are known in the art and are commercially available. They may be incorporated as "prills" "marumes" or suspensions.

The fluorescent agents which can be used in the liquid cleaning products according to the invention are well known and many such fluorescent agents are available commercially. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in a detergent composition is generally from 0.02-2% by weight.

When it is desired to include anti-redeposition agents in the liquid cleaning products, the amount thereof is normally from about 0.1% to about 5% by weight, preferably from about 0.2% to about 2.5% by weight of the total liquid composition. Preferred anti-redeposition agents include carboxy derivatives of sugars and celluloses, e.g. sodium carboxymethyl cellulose, anionic poly-electrolytes, especially polymeric aliphatic carboxylates, or organic phosphonates.

When it is desired to include a bleach catalyst, a manganese complex as described in Applicants' co-pending European Patent Application No. 91201171.5 and No. 91201172.3 can be used in an amount

corresponding to a manganese level of from 0.0001 to about 1.0% by weight, preferably from 0.0005 to 0.5% by weight.

WATER

The compositions are substantially non-aqueous, i.e. they contain little or no free water, preferably no more than 5%, preferably less than 3%, especially less than 1% by weight of the total composition. It has been found that the higher the water content, the more likely it is for the viscosity to be too high, or even for setting to occur.

USE

Composition in accordance with the present invention may be used for several detergency purposes, for example the cleaning of surfaces and the washing of fabrics. For the washing of fabrics, preferably an aqueous liquor containing 0.1 to 10 %, more preferably 0.2 to 2%, of the non-aqueous detergent composition of the invention is used.

PROCESSING

During manufacture, it is preferred that all raw materials should be dry and (in the case of hydratable salts) in a low hydration state, e.g. anhydrous phosphate builder, sodium perborate monohydrate and dry calcite abrasive, where these are employed in the composition. In a preferred process, the dry, substantially anhydrous solids are blended with the liquid phase in a dry vessel. If deflocculant materials are used, these should preferably -at least partly- be mixed with the liquid phase, prior to the addition of the solids. In order to minimise the rate of sedimentation of the solids, this blend is passed through a grinding mill or a combination of mills, e.g. a colloid mill, a corundum disc mill, a horizontal or vertical agitated ball mill, to achieve a particle size of 0.1 to 100 µm, preferably 0.5 to 50 µm, ideally 1 to 10 µm. A preferred combination of such mills is a colloid mill followed by a horizontal ball mill since these can be operated under the conditions required to provide a narrow size distribution in the final product. Of course particulate material already having the desired particle size need not be subjected to this procedure and if desired, can be incorporated during a later stage of processing.

During this milling procedure, the energy input results in a temperature rise in the product and the liberation of air entrapped in or between the particles of the solid ingredients. It is therefore highly desirable to mix any heat sensitive ingredients into the product after the milling stage and a subsequent cooling step. It may also be desirable to de-aerate the product before addition of these (usually minor) ingredients and optionally, at any other stage of the process. Typical ingredients which might be added at this stage are perfumes and enzymes, but might also include highly temperature sensitive bleach components or volatile solvent components which may be desirable in the final composition. However, it is especially preferred that volatile material be introduced after any step of deaeration. Suitable equipment for cooling (e.g. heat exchangers) and de-aeration will be known to those skilled in the art.

For ensuring that clay material, if used in the composition, consist of platelet shaped particles of the desired particle size it is preferred to mix the clay materials into the compositions under high shear conditions.

It follows that all equipment used in this process should preferably be completely dry, special care being taken after any cleaning operations. The same is true for subsequent storage and packing equipment.

Example A

The molar solubilities of precursor active groups are summarised below for a number of peracid precursors. These data refer to the solubility found in the liquid phase, i.e. the 2:1 nonionic surfactant combination of only (Vista NI® and Synperonic A3) of the composition of Example 1 below, at ambient temperature. The nonionic blend contains a small amount of residual water which has a finite influence on the measured solubilities.

Table I

Precursor Solubility				
Precursor mw	No. active groups	Precursor*)	% w/w dissolved	mmol% active groups dissolved
349	1	Compound A	<0.05	<0.14
303	1	Compound B	<0.025	<0.08
300	1	Compound C	0.3	1.0
335	1	Compound E	<0.01	<0.03
329	1	Compound F	<0.025	<0.08
228	2	TAED**)	0.18	1.6
336	1	SNOBS**)	1.11	3.3

*) Designations as hereinbefore defined.
**) Comparative examples.

The solubility data shown in Table I were obtained by GC analysis (TAED) and by HPLC (rest). NMR and titration data are consistent with the TAED figure.

Example 1

The following formulation containing various types of precursors was tested for percarbonate and precursor stability:

	Parts by wt
Vista NI® (1)	28
Synperonic A3® (2)	14
Sipernat D17®	3
Marlon AS3® (3)	6
$CaCO_3$	6
Precursor	3.4
Percarbonate (4)	20
	80.4

(1) a C_{10} – C_{12} alcohol ethoxylated with an average of 6.5 ethylene oxide groups per molecule, ex Vista
(2) a C_{13} – C_{15} alcohol ethoxylated with an average of 3 ethylene oxide groups per molecule, ex ICI
(3) dodecyl sulphonic acid, added in free acid form
(4) Sodium percarbonate, 7.5% active oxygen ex FMC

The results are given in the following table.

precursor	stability precursor	stability percarbonate
compound A	88% **)	88% **)
compound B	90% *)	90 *)
compound C	35% *)	90% *)

*) storage stability after storage for 4 weeks at ambient temperature
**) storage stability after storage for 8 weeks at ambient temperature.

EXAMPLE 2

To illustrate the magnitude of the benefits for different insoluble precursors over those that have a significant solubility in nonionic, the following base formulation was prepared with four different precursors. The measured stability in each case is as shown.

Formulation	
	Parts
Nonionic (1)	42
Percarbonate (2)	10
Precursor	3

Stability	
Precursor (designations as hereinbefore defined)	Stability of the precursor at 37 ° C (3)
TAED	t0.5 = 6 days (4)
SNOBS	t0.5 = 4 days (4)
Compound B	> 80% available after 4 weeks
Compound C	> 80% available after 4 weeks
Compound F	94% available after 1 week

(3) The stability data shown were obtained by GC analysis and by HPLC.
(4) t0.5 = decay half life

Claims

1. A substantially non - aqueous liquid cleaning composition comprising a non - aqueous liquid phase and dispersed solids which comprise an inorganic percarbonate bleach and a precursor, wherein the precursor has a molar solubility in the liquid phase alone multiplied by the number of active groups of no more than 1.2 mmol per 100 ml at 25 ° C.

2. A composition according to claim 1, wherein said molar solubility multiplied by the number of active groups is no more than 0.2 mmol per 100ml at 25 ° C.

3. A composition according to claim 1, wherein the precursor is a percarboxylic acid precursor.

4. A composition according to claim 1, wherein the precursor is a cationic compound.

5. A composition according to claim 1, wherein the precursor is 1 - [4 - (N,N,N - trimethylammonium - methyl)benzoyloxy] benzene - 4 - sulphonate.

6. A composition according to claim 1, wherein the precursor is 2 - (N,N,N - trimethylammonium)ethyl sodium 4 - sulphophenyl carbonate.

7. A composition according to claim 1, wherein the precursor is sodium benzoyloxy benzene sulphonate.

8. A composition according to claim 1, wherein the precursor is a poly - diacetylallylamine.

(1) a C_{16} - C_{12} alcohol ethoxylated with an average of 6.5 ethylene oxide groups per molecule, ex Vista

(2) sodium percarbonate, 15% active oxygen, ex Interox